Research Article

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Influence of unburned pulverized coal on gasification reaction of coke in blast furnace

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Abstract: In order to explore the influence of unburned pulverized coal on gasification reaction of coke in blast furnace, kinetic rules of gasification reaction between CO_2 and coke powder adding pulverized coals with different volatiles were studied by thermogravimetric analysis. The results showed that weight-loss ratio of samples reacted with CO_2 increased after adding pulverized coal, and the weight-loss ratio rose with the increase of coal's addition. When the content of pulverized coal was up to 50%, the weight-loss ratio of the sample which adding pulverized coal with high volatile was higher under the same temperature. The activation energy about C- CO_2 gasification reaction of samples reduced observably after adding pulverized coal. The activation energy of samples had a largest decrease with $83.408 \text{ kJ mol}^{-1}$ at the range of 1223 K~1373 K and it was $28.97 \text{ kJ mol}^{-1}$ at the range of 1373 K~1523 K. The addition of pulverized coal with high volatile can reduce the reaction activation energy of samples more effectively. In the soft melting zone, the gasification reaction model of coke blocks attached the unburned pulverized coal was up to unreacted core model and porous volume-reacted model jointly.

Keywords: unburnt pulverized coal; coke; carbon solution loss reaction; reactivity; kinetics

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List of symbols

β	Heating rate, $\beta = \frac{dT}{dt}$;
$\frac{d\alpha}{dt}$	Reaction rate;
A	Pre-exponential factor;
E	Reaction activation energy;
$f(\alpha)$	Weightlessness function;
k	Constant of reaction rate;
n	Reaction order;
R	Ideal gas constant, $8.314 \text{ J/K}\cdot\text{mol}$;
ω_0	Sample mass before reaction;
ω_∞	Residual mass after reaction;
ω_t	Sample mass at time t ;
T_0	Initial reaction temperature

1 Introduction

Pulverized coal injection in blast furnace is the effective way to reduce coke consumption and fuel ratio, while a certain extent, reduce the environmental pollution caused by coking. Currently, due to the cost efficiency of every steel companies is the impending event, pulverized coal injection ratio is improving. Under the conditions of the large coal injection ratio, pulverized coal is injected at a high speed through the tuyere, and the time of coal pyrolysis and char combustion is very short (about 20ms) in raceway. Therefore the residual coke is not fired, and the unburned char will react with other substances further in the blast furnace [1–3]. Figure 1 is a schematic about consumption way of pulverized coal when it was injected into the blast furnace. Some papers pointed out that [4, 5] the reaction

Figure 1: Consumption of pulverized coal in blast furnace

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Table 1: Ultimate analysis and ultimate analysis of anthracite

	Proximate analysis, ad/(%mass)			Ultimate analysis, ad/(%mass)				
	Volatile	Ash	Fixed Carbon	C	H	N	O	S
1#Coal	9.31	7.54	83.15	85.42	3.06	0.80	1.82	0.24
2#Coal	13.63	9.65	76.72	79.32	3.70	0.70	5.80	0.62

Table 2: Proportion scheme of experimental sample

No.	Proportion	No.	Proportion
1	Coke: 1#Coal=9: 1	4	Coke: 2#Coal=9: 1
2	Coke: 1#Coal=7: 3	5	Coke: 2#Coal=7: 3
3	Coke: 1#Coal=1: 1	6	Coke: 2#Coal=1: 1

between unburned pulverized coal and CO_2 is happened in the vicinity of coke layer in the cohesive zone.

Coke in the blast furnace is act as a heat source, reducing agent, carburizing agent involved in physical and chemical reactions in furnace. More importantly, it also plays the role of the skeleton supporting the burden. The smelting process was strengthened by pulverized coal injection representatively, and the residence time of coke in blast furnace especially in deadman is prolonged. Under these conditions, coke experienced greater damaging effects, the coke layer became thinner, and "coke window" layer of cohesive zone which is maintained permeability became smaller. So the skeleton effect of coke is particularly important [6–10].

The role of coke in the blast furnace skeleton is good or bad, depends both on the quality of coke and smelting process of blast furnace. Numerous studies showed that the pulverization of coke in the furnace is the root cause of permeability deterioration. The pulverization of coke in the blast furnace is mainly due to the occurrence of solution loss reaction with CO_2 . With the increase of the amount of pulverized coal injection, the number of unburned pulverized coal in raceway was increasing, and therefore the impact of unburned pulverized coal to gasification reaction of coke cannot be ignored [11]. This article studied the reaction behavior of coexistence of unburned pulverized coal and coke with CO_2 by thermal gravimetric analysis.

2 Experimental

The coke and coal of a 3200m^3 blast furnace were selected for the experiment. The coke reactivity index (CRI) is 27.7% and coke strength after reduction (CSR) is 63.83%. In order to compare the influence of unburned pulverized coal

to gasification reaction of coke after pulverized coal with different volatile matter injected, two kinds of pulverized coals were selected. Their proximate analysis and ultimate analysis are shown in Table 1.

The coke and coal mentioned above were made into powder, their particle sizes were controled at 0.074mm or less. Before the test, pulverized coal and coke should be mixed uniformly according to a certain proportion: coal's quality accounted for 10%, 30%, 50% the mixed sample's quality and the specific mixing scheme is shown in Table 2.

Experiments conducted through the thermo gravimetric analyzer (TGA) of NETZSCH. The system collected samples automatically, and the weight-loss curves were plotted by the computer. 18mg of every experimental sample was weighed and placed on the heat balance. Then the temperature of samples were raised from indoor temperature to 973 K in argon gas atmosphere at the heating rate of 293 K/min to remove volatile. The unburned pulverized coal appeared in this process. When the temperature reached 973K, CO_2 gas was needed for further heating up from 973 K to 1523 K at the heating rate of 288 K/min to make carbon solution loss reaction conduct adequately. At the same time, the coke powder without pulverized coal was experimented repeatedly to compare the impact of unburned pulverized coal to solution loss reaction of coke.

3 Results and discussion

3.1 Weight-loss rate of the sample reacts with CO_2

Hu's study has shown that [12], the solution loss reaction of coke began to occur at 1073 K and carbon solution loss reaction was taken place in a certain temperature range. Due to the various volatile of different test samples, the initial quality of test samples was different when they react with CO_2 at 973 K. So the different effects of addition of pulverized coal to coke can be compared by weight-loss rate. The curves of weight-loss rate at different temperature obtained from thermogravimetric experiment are shown in Figure 2.

Table 3: Weight-loss rate of pulverized coal and coke separately at different temperatures

Temperature (K)		1173	1223	1273	1323	1373	1423	1473
Weight-loss	1#Coal	1.660	4.280	8.380	16.454	31.616	48.498	66.561
Rate	2#Coal	3.197	6.578	11.304	19.98	34.405	50.876	68.197
%	Coke	0.037	1.315	4.078	10.515	20.678	31.592	44.853

Figure 2: Weight-loss rate curves of gasification reaction on char- CO_2

Weight-loss rate curves were based on the actual quality of the samples at 1023 K. As the temperature rose, the samples gradually reacted with CO_2 , and the weight-loss value increased. As can be seen from Figure 2, after the pulverized coal adding into coke powder, the weight-loss rate increased at the same temperature. And with the increase of the content of pulverized coal, this trend became even more obvious. Meanwhile, the effects of pulverized coals with different volatile to reaction weight-loss rate of samples were different. When the content of pulverized coal was 10% or 30%, the effect on weight-loss rate of the sample was little. But when the content was 50%, the weight-loss rate of the sample containing high volatile pulverized coal was greater at the same temperature.

In order to explore the reasons for the increase of weight-loss rate after adding pulverized coal, the two pulverized coals were used to do the same gasification reaction experiment solely. According to the TGA experimental data, the weight-loss rates of the two pulverized coals reacted with CO_2 at different temperatures were obtained. Table 3 lists the weight-loss rates of 100% pulverized coal and 100% coke powder from 1173 K to 1473 K.

Due to the huge difference in the reactivity, it can be considered that the unburned pulverized coal and the coke powder reacted with CO_2 relatively and independently in

mixed samples. From Table 3, it is clearly observed that the weight-loss rate of the pulverized coal reacted with CO_2 is far greater than the coke at the same temperature. And the weight-loss rate of the pulverized coal with high volatile is greater than the low volatile pulverized coal. Therefore, the weight loss of mixed sample with coal and coke is caused by the gasification reaction between unburned pulverized coal and CO_2 . This shows that the unburned pulverized coal is a protective effect on gasification reaction of coke. Because of the detrainment of volatile can make the porosity of pulverized coal be larger, so the specific surface area of the unburned pulverized coal made from the coal with the higher volatile is large. The reactivity of this unburned pulverized coal reacting with CO_2 is high. It can be concluded that when injected the high volatile pulverized coal into blast furnace, the reaction of unburned pulverized coal with CO_2 is taken part in the upper of cohesive zone sufficiently, and it can play a better protective effect to the degradation of coke.

3.2 Kinetics analysis of gasification reaction

According to the experimental weight-loss curves, the rate of weight-loss change (α) can be determined when the reaction has proceeded to a certain time (t):

$$\alpha = \frac{\omega_0 - \omega_t}{\omega_0 - \omega_\infty} \quad (1)$$

As the gas flow of CO_2 was constant in the experiment, and the reaction was under atmospheric pressure, so the P_{CO_2} is a constant. According to the rate equation of gasification reaction of char- CO_2 (2) and the Arrhenius Equation (3), the general form of kinetic Equation (4) can be obtained.

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (2)$$

$$k = A \cdot e^{-\frac{E}{RT}} \quad (3)$$

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}} (1 - \alpha)^n = \frac{A}{\beta} e^{-\frac{E}{RT}} f(\alpha) \quad (4)$$

Table 4: Kinetics calculation of carbon dissolving reaction

Proportion	Temperature interval (K)	Fitting curve ($Y=aX+b$)	Similarity (R^2)	Activation energy(E)/kJ·mol ⁻¹
Coke	1223~1373	$Y=246644X+5.7977$	0.9972	246.644
	1373~1523	$Y=137272X-3.8948$	0.9993	137.272
Coke+10%1#coal	1223~1373	$Y=236362X+6.7821$	0.9972	236.362
	1373~1523	$Y=115060X-5.6522$	0.9957	115.060
Coke+30%1#coal	1223~1373	$Y=221245X+4.0099$	0.9985	221.245
	1373~1523	$Y=110222X-5.8047$	0.9904	110.222
Coke+50%1#coal	1223~1373	$Y=202208X+2.1832$	0.9998	202.208
	1373~1523	$Y=108302X-5.869$	0.9861	108.302
Coke+10%2#coal	1223~1373	$Y=196140X+1.4593$	0.9989	196.140
	1373~1523	$Y=114838X-5.6674$	0.9992	114.838
Coke+30%2#coal	1223~1373	$Y=187723X+0.8508$	0.9975	187.723
	1373~1523	$Y=116178X-5.3395$	0.9930	116.178
Coke+50%2#coal	1223~1373	$Y=163236X-1.0501$	0.9956	163.236
	1373~1523	$Y=119195X-4.8258$	0.9927	119.195

The kinetic parameters calculated from the above equations are the apparent kinetic parameters of experience.

There are many computing method of kinetic parameters deduced from the general form of kinetic equations [13–16]. This article used the integral method of Coats-Redfern, using the non-isothermal method of a single procedure of temperature control. That is to say the heating rate (β) is a constant. After solving the integral on both sides of the Equation (4) and set the initial state of the equation ($\alpha = 0$, $T = T_0$), the Equation (5) was obtained as follow.

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T e^{-\frac{E}{RT}} dT \quad (5)$$

The reaction rate at the low temperature is negligible usually. So that the Equation (5) becomes:

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{-\frac{E}{RT}} dT \quad (6)$$

Make the definition: $g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)}$, and the gasification reaction of C-CO₂ can be described as a first-order reaction [17, 18]. So the reaction order $n=1$, and $f(\alpha) = 1 - \alpha$, the Equation (6) becomes:

$$g(\alpha) = \frac{ART^2}{\beta E} \left[1 - \frac{2RT}{E} \right] e^{-\frac{E}{RT}} \quad (7)$$

After solving the natural logarithm on both sides of the Equation (7):

$$\ln \left[\frac{g(\alpha)}{T^2} \right] = \ln \left\{ \frac{AR}{\beta E} \left[1 - \frac{2RT}{E} \right] \right\} - \frac{E}{RT} \quad (8)$$

During the experiments, the heating rate was determined ($\beta = 288$ K/min). Therefore, the reaction temperature, and most typically in terms of E , the value of $\ln \left\{ \frac{AR}{\beta E} \left[1 - \frac{2RT}{E} \right] \right\}$ is a constant. Set up $X = \frac{1}{T}$, $Y = \ln \left[\frac{g(\alpha)}{T^2} \right]$, the approximate line can be obtained by plotting to X-Y, and the activation energy(E) and the pre-exponential factor (A) can be calculated by Equation (7). Results of kinetics calculation are shown in Table 4.

To study the relationship between the content of pulverized coal in the samples and changes of activation energy, the data of Table 4 were plotted. Figure 3 shows that in the two temperature ranges of 1223 K~1373 K and 1373 K~1523 K, the activation energy of coke sample is the largest. After adding coal, the activation energy of the sample is significantly reduced. It shows that the reactivity of the sample becomes larger after adding coal.

At the same time, it can be seen that the activation energy in the temperature range of 1223 K~1373 K is generally greater than it in the temperature range of 1373 K~1523 K. This suggests that the carbon solution loss reaction in the temperature range of 1373 K~1523 K is more vigorous. In the temperature range of 1223 K~1373 K, the activation energy of samples reduced with the increase of the content of the pulverized coal, and the activation energy of samples added in 2#coal had the greater decrease. The results show that the different volatile contents of the coal have significant influence on the activation energy of the gasification reaction between pulverized coal and CO₂, and the higher volatile content, the smaller the activation energy. In the temperature range of 1373 K~1523 K, the activation

(0% content of coal is equal to 100% coke)

Figure 3: Relationship between reaction activation energy and the additive amount of coal

energy also reduced with the increase of the content of the pulverized coal, but the extent of decrease was not obvious, and the activation energy of samples added two coals was nearly. This is because when the reaction was carried out above 1373 K, the pulverized coal of reaction was gradually consumed, and more and more coke powders involved in the reaction. Especially to the samples added 2# coal, since the high volatile of the coal and the low content of fixed carbon, when the reaction proceeded to certain extent, the amount of coke participating in the reaction increased, and the reaction activation energy of the sample became larger slightly.

3.3 Kinetics model of gasification reaction

In smelting process of blast furnace, the unburned pulverized coal was brought to the cohesive zone with the rising gas. As the small granularity, huge specific surface area, the high reactivity with CO_2 , so the unburned pulverized coal will react with CO_2 ahead of the coke. There are two reaction zones of the unburned pulverized coal reacted with CO_2 : one is in the atmosphere rising along with gas flow at a certain temperature, and the alternative is in the surface of the coke and ore. Some of the unburned pulverized coal can be attached to the surface of the coke and ore through the gas stream and react with CO_2 in these places.

For gas-solid reaction, there are varieties of kinetic models in the field of metallurgy [19, 20]. For the solid blocks or the blocks with low porosity and the solid materials with the big difference of reactivity between the kernel and the interface, we usually use the unreacted core model. The unreacted core model is a non-catalytic gas-solid re-

(C_0 , C_1 and C_2 indicate the gas concentration of CO_2 in different radial position, $C_0 > C_1 > C_2$)

Figure 4: Gasification reaction model of coke blocks attached the unburnt pulverized coal

action model. During the reaction, the particle size does not change, and the core does not react, but the reaction interface continues to push toward the core. For the solid materials with high porosity or the ore balls, we usually use the porous volume-reacted model. In porous volume-reacted model, while the reactive gases are diffused into the solid materials with high porosity, they also take place the chemical reaction in the pore. That is to say, the diffusion and the chemical reaction are processed simultaneously. When the unburned pulverized coal is attached to the surface of the porous coke, the model of coke solution loss reaction is shown in Figure 4.

CO_2 in the furnace gas can diffuse into the interior of coke. The gasification reaction is carried out not only on the surface but also inside coke and it is processed with the gas diffusion at the same time. Generally, when the temperature is low, the restrictive link is chemical reaction and CO_2 can be sufficiently diffused into the interior of the porous coke. When the temperature rises, the reaction rate becomes large, CO_2 diffusion only to a certain depth, and the reaction will be carried out within a certain radius. When the temperature is higher, the chemical reaction rate is very high, and CO_2 is almost completely consumed on the surface of the coke, the reaction performed only on the surface [21, 22]. When the coke blocks attached the unburned pulverized coal, the reaction of coke- CO_2 can be seen as the unreacted core model. The reaction was occurred in the surface adequately, and solution loss of the

coke's kernel is small. Meanwhile, as the uneven attachment of the unburned pulverized coal, a small amount of CO₂ can penetrate into the interior of coke through the pores, then the gasification reaction follows the porous volume-reacted model.

4 Conclusion

- (1) Weight-loss ratio of samples reacted with CO₂ increased after adding pulverized coal, and the weight-loss ratio rose with the increase of coal's addition.
- (2) When the content of pulverized coal was small, the volatile of coal had little influence on the weight-loss ratio of samples; when the content of pulverized coal was 50%, the weight-loss ratio of the sample which added pulverized coal with high volatile was higher under the same temperature.
- (3) The activation energy of samples had the largest decrease with 83.408 kJ·mol⁻¹ at the range of 1223 K~1373 K and it was 28.97 kJ·mol⁻¹ at the range of 1373 K~1523 K.
- (4) The addition of pulverized coal with high volatile can reduce the reaction activation energy of samples more effectively. Due to the larger reactivity, the unburned pulverized coal of it reacted with CO₂ before coke, and the CO₂ in the atmosphere was consumed simultaneously. So the appropriate pulverized coal injection with high volatile can cut down the coke degradation in blast furnace.
- (5) Near the soft melting zone, the gasification reaction model of coke blocks attached the unburned pulverized coal was up to unreacted core model and porous volume-reacted model jointly.

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